

Polymer Pendant Crown Thioethers for Removal of Mercury from Acidic Wastes: Synthesis, Characterization and Application

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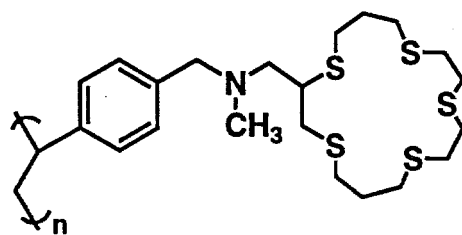
ABSTRACT

Removal of mercury ions from industrial waste streams is a difficult and expensive problem requiring an efficient and selective extractant that is resistant to corrosive conditions. We have now developed an acid-resistant thiacyclopentadiene polymer that has potential utility as a selective and cost-effective Hg^{2+} extractant. Copolymerization of a novel C-substituted thiacyclopentadiene, N,N-(4-vinylbenzylmethyl)-2-aminomethyl-1,4,8,11,14-pentathiacycloheptadecane, with DVB (80% divinylbenzene) using a radical initiator generated a highly cross-linked polymer containing pendant thiacyclopentadienes. Mercury extraction capabilities of the polymer were tested in acidic media (pH range: 1.5 to 6.2) and the extraction of Hg^{2+} was determined to be 95% at a mixing time of 30 minutes. The thiacyclopentadiene polymer was also determined to be selective for Hg^{2+} , even in the presence of high concentrations of competing ions such as Pb^{2+} , Cd^{2+} , Al^{3+} , and Fe^{3+} . The bound Hg^{2+} ions can then be stripped from the polymer, allowing the polymer to be reused without significant loss of loading capacity. The binding of Hg^{2+} to the polymer has been examined by X-ray photoemission spectroscopy. The thiacyclopentadiene appears unaffected by incorporation into the polymer and the Hg^{2+} appears to be bound to the polymer complex in a similar manner as Hg^{2+} is bound in monomeric thiacyclopentadienes containing five sulfur atoms.

INTRODUCTION

Due to increased environmental concerns about waste remediation, major efforts are under way to design new materials that can effectively remove and recover toxic metal ions from aqueous solutions. One approach to this problem has been to utilize organic ligands anchored to solid supports.^{1,2} Such a strategy presents several advantages. Specific binding properties of the ligands can be exploited to selectively remove a desired metal ion from a complex solution of cations. These materials can also be recycled and reused to make the treatment process cost-effective. In addition, this technique can potentially minimize the amount of secondary waste generated in the extraction process, a major challenge in waste treatment. The utility of these anchored organic ligands, or polymer-pendant ligands, has been demonstrated for the extraction of a variety of metal ions from aqueous media.³⁻⁷

Inset.



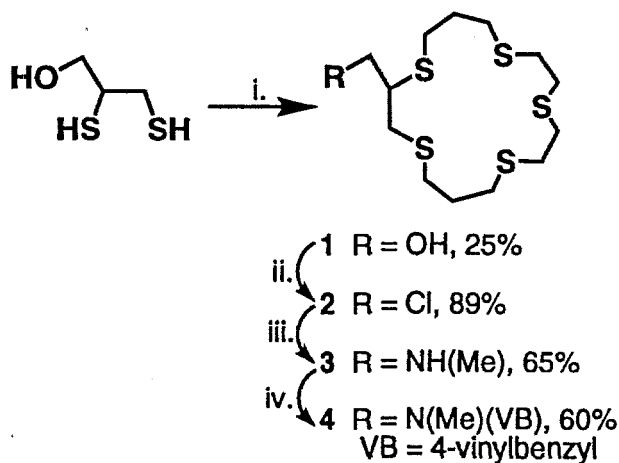
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We have been interested in designing polymer-bound extractants for Hg^{2+} remediation in mixed waste streams generated at U.S. Department of Energy facilities. Some of these waste streams are not only very acidic, but also contain a wide variety of other metal ions, such as Al^{3+} , Fe^{3+} , and Pb^{2+} . Removal of Hg^{2+} thus requires a robust and selective sequestering agent. To address this problem, we have synthesized polymer-pendant crown thioethers (thiacrowns) for the selective removal of Hg^{2+} from acidic aqueous media (**Inset**).⁸ Thiacrowns⁹ are well suited for this task due to the high affinity that sulfur crowns have for the Hg^{2+} ion^{10–12} as well as their resistance to degradation under acidic conditions.¹³ As pendant ligands on solid supports, thiacrowns have been shown to remove soft metal ions, such as Ag^+ , Hg^{2+} and Pb^{2+} , directly from aqueous solutions.^{14–17} In this paper we summarize the synthesis, characterization and extraction capabilities of the polymer-pendant thiacrown towards removal of mercury in aqueous acidic mixtures devised to simulate real waste streams, such as fuel reprocessing streams.

EXPERIMENTAL

Synthesis. The synthesis of the [17]aneS₅-polymer has been previously described.^{8,18} Scheme 1 summarizes the preparation of thiacrown polymer precursor. Copolymerization of pendant arm crown **4** and divinylbenzene using a radical initiator (AIBN) generated the highly cross-linked thiacrown polymer **5**. Elemental analysis of **5** showed that each gram of the polymer contained 1.5 mmol of thiacrown (based on % by weight of sulfur).

Scheme 1. Reagents and Conditions: i. $\text{S}(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{OTs})_2$, Cs_2CO_3 , DMF, 90°C ; ii. SOCl_2 , CH_2Cl_2 , RT; iii. MeNH_2 , Na_2CO_3 , MeCN, 0°C ; iv. 4-vinylbenzyl chloride, Na_2CO_3 , MeCN, 81°C .



Extractions. The conditions for the Hg^{2+} extraction and recycling experiments have been previously reported.^{18,19} The thiacrown polymer (20 mg) was mixed with solutions (5 mL) of mercury nitrate at various pH values and Hg^{2+} concentrations for a variety of mixing times. For metal ion competition studies, a known concentration of the competing ion was added to the extraction solution. After the mixing was complete, the polymer was filtered and the concentration of Hg^{2+} remaining in solution was determined spectrophotometrically. This was performed by extracting the aqueous solution with a solution of diphenylthiocarbazone (dithizone or dtz) in CHCl_3 and determining the $\text{Hg}(\text{dtz})_2$ [$\text{Hg}(\text{C}_{13}\text{H}_{11}\text{N}_4\text{S})_2$] content at $\lambda_{\text{max}} = 490$ nm. For the polymer recycling experiment, the Hg^{2+} -loaded polymer was washed with acetone to remove residual water and dried. The polymer was then treated with Hdtz in CHCl_3 , filtered and washed with CHCl_3 to remove the $\text{Hg}(\text{dtz})_2$ complex. The dried thiacrown polymer could then be used to extract more Hg^{2+} without a significant loss of loading capacity.

Characterization. X-ray photoemission spectroscopy (XPS) was utilized to characterize the binding of Hg to the polymer. A full analysis has been reported elsewhere.²⁰ For the approach used for the analyses, the following model compounds were purchased or synthesized: $\text{Hg}(\text{SC}(\text{N}_2\text{HC}_6\text{H}_5)(\text{N}_2\text{C}_6\text{H}_5))_2$, ($\text{Hg}(\text{dtz})_2$); the uncomplexed ligand, diphenylthiocarbazone (Hdtz); 1,4,7,10,13,16-hexathiacyclooctadecane, ([18]aneS₆); $\text{NaS}_2\text{CN}(\text{C}_2\text{H}_5)_2$, (NaEt_2dtc); $\text{Hg}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_2$, ($\text{Hg}(\text{dtc})_2$); 1,4,7,10,13-pentathiacyclopentadecane, ([15]aneS₅); $\text{Hg}(1,4,7,10,13\text{-pentathiacyclopentadecane})(\text{PF}_6)_2$, ($\text{Hg}[15]\text{aneS}_5$); $\text{Hg}(1,4,7,10,13,16\text{-hexathiacyclooctadecane})(\text{PF}_6)_2$, ($\text{Hg}[18]\text{aneS}_6$); $\text{Hg}[17]\text{aneS}_5\text{-OH}$; the mercury bound polymer $\text{Hg}[17]\text{aneS}_5\text{-polymer}$, **5**, (generated by methods described above through extraction of Hg^{2+} from acid mercury nitrate solutions by [17]aneS₅-polymer).^{8,20-23}

XPS experiments were performed on a Physical Electronics 5400 ESCA system using Mg K α radiation (1253.6 eV) and a hemispherical analyzer pass energy of 17.90 eV giving an overall energy resolution of 1.1 eV. All binding energies are referenced to the Fermi level of the analytical instrument as calibrated to the Au 4f peaks. Binding energies were further referenced to the C 1s photoelectron line arising from adventitious carbon at 284.6 eV

to account for charging effects. The powder samples were pressed into indium foil and attached to the sample holder, which was then introduced into the ultra-high vacuum chamber for analysis.

RESULTS

Reaction times for [17]aneS₅-polymer. Table 1 shows the Hg²⁺ extraction results for thiacycrown polymer **5** at pH 3.6 at various reaction times. The data clearly shows that the polymer is very efficient for the removal of Hg²⁺ for reaction times as short as 30 minutes. Shorter reaction times were not possible due to experimental limitations.

Table 1. Extraction of Hg²⁺ from aqueous solution by thiacycrown polymer as a function of time.^a

Initial Hg ²⁺ Concentration, ppm	Reaction Time, h	Percent Extraction
4.3	18	98
4.3	3	95
4.3	1	95
4.3	0.5	95
34	0.5	99

^aEach extraction was carried out at pH 3.6.

^bExtraction (%) = 100 – ([remaining Hg²⁺]/[starting Hg²⁺] x 100).

Table 2. Extraction of Hg²⁺ from aqueous solution by **5** as a function of pH.

Initial Hg ²⁺ Concentration, ppm	pH	Percent Extraction
3.7	1.45	99
4.1	2.59	99
4.3	3.60	98
3.5	6.12	97
32	1.49	99
34	2.58	98
34	3.60	99
32	6.12	97
170	1.45	91
400	2.58	50

^aEach extraction was stirred for 30 minutes.

^bExtraction (%) = 100 – ([remaining Hg²⁺]/[starting Hg²⁺] x 100).

Hg²⁺ uptake for [17]aneS₅-polymer. Table 2 summarizes the Hg²⁺ extraction results as a function of pH and Hg²⁺ concentrations. Again, the data shows that the polymer is very effective in extracting Hg²⁺ from aqueous solution in the pH range of 1.5 to 6.1 at concentrations of 4 and 30 ppm. The polymer is also effective in removing Hg²⁺ concentrations of 4 ppm to 200 ppm at low pH. To ascertain Hg²⁺ binding capacity of the resin, polymer **5** was treated with 400 ppm of Hg²⁺ at pH 2.5 and the results show that only 50% of the Hg²⁺ was extracted from solution. From this type of experiment, it was determined that the resin has ~0.5 mmol of Hg²⁺ binding sites per gram resin. Assuming that each Hg²⁺ ion complexes with a single crown, that number suggests that only ~30% of the thiacycrowns are involved in Hg²⁺ extraction. This number may be higher, however, since there could be cooperative

binding of the Hg^{2+} ions, meaning that sulfur donors from two or more crowns may be involved in binding a single Hg^{2+} ion. However, this does not seem to be the case based on the XPS results below.

Selectivity of [17]aneS₅-polymer. The selectivity of polymer **5** for Hg^{2+} was tested in the presence of competing metal ions (Al^{3+} , Cd^{2+} , Fe^{3+} , Pb^{2+}) and the results are summarized in Table 3. The data shows that the thiacyclopentane polymer preferentially binds Hg^{2+} even at large molar ratios of competing metal ions.

Table 3. Hg^{2+} ion selectivity data for thiacyclopentane polymer^a

Metal	pH	Molar Ratio ($\text{M}^{n+}/\text{Hg}^{2+}$)	Percent Extraction ^b
Pb^{2+}	1.40	5	98
Cd^{2+}	1.51	5	97
Fe^{3+}	1.53	10	98
Al^{3+}	1.62	100	95

^aEach extraction was stirred for 30 minutes.

^bExtraction (%) = $100 - ([\text{remaining } \text{Hg}^{2+}]/[\text{starting } \text{Hg}^{2+}] \times 100)$.

Regeneration of [17]aneS₅-polymer. Polymer **5** was regenerated through the treatment of the Hg^{2+} -loaded polymer with dithizone in CHCl_3 . The dried, regenerated polymer was exposed to a 40 ppm Hg^{2+} solution and reacted for 30 min. The residual Hg^{2+} in the solution was found to be < 1 ppm, indicating no loss in activity. While this procedure may not be the ideal method to regenerate the polymer, it does show that polymer **5** can be stripped of the bound Hg^{2+} and then reused without degradation, for at least one cycle.

Hg binding to [17]aneS₅-polymer. To establish the nature of the Hg^{2+} binding sites in the polymer, several model compounds with S-containing ligands and their corresponding Hg^{2+} complexes were examined by XPS.²⁰ This approach relies on fully understanding the binding in these model compounds, relating their single crystal x-ray structures with spectroscopic behavior, then applying this behavior to solids where single crystal x-ray data can not be obtained, as in amorphous polymers. The XPS experiment uses x-rays to eject electrons from non-valence shells, and the resulting energy spectra can indicate details of the binding around the atom being examined. In this work, the energies of interest are the $4f_{7/2,5/2}$ pair for Hg and $2p_{3/2,1/2}$ pair for S.

Figure 1 shows the $4f_{7/2,5/2}$ spectra for the [17]aneS₅-polymer after exposure to the Hg^{2+} solution along with two Hg^{2+} thiacyclopentane compounds. The positions for each material are almost identical, suggesting the Hg^{2+} is bound to the polymer in a similar mode as $\text{Hg}[15]\text{aneS}_5$, a known model compound. However, comparisons with $4f_{7/2,5/2}$ XPS spectra of other Hg^{2+} compounds (including non-sulfur type) show these positions do not vary significantly.²⁴⁻³¹

Figure 2 shows the deconvoluted S 2p spectra for [17]aneS₅-polymer, the polymer after exposure to the Hg^{2+} solution, and two other thiacyclopentane compounds with and without mercury. The spectra show one set of $2p_{3/2,1/2}$ energies for the uncomplexed ligands, and two sets of $2p_{3/2,1/2}$ energies for the Hg complexes. These energies are further documented in Table 4 for several compounds where the sets of the $2p_{3/2,1/2}$ energies are related to the type of

S bonding. In all these compounds, the effect of the binding of Hg is evident by a systematic shift of an additionally produced set of energies.

This additional information from the S $2p_{3/2,1/2}$ energies combined with the Hg $4f_{7/2,5/2}$ energies indicates the following about the binding sites in the polymer: 1) the [17]aneS₅ thiacyclopentane ring is unaffected by incorporation into the polymer, and 2) the mercury appears to be bound to the polymer complex in a similar manner as mercury is bound in [15]aneS₅ and other thiacyclopentanes containing five sulfur atoms. The Hg²⁺ is probably bound to all five sulfur atoms (thioethers) of the thiacyclopentane giving a distorted square-based pyramidal stereochemistry, as in the case of [15]aneS₅.²¹ This can be best pictured as a baseball fitting into a baseball glove.

CONCLUSIONS

A novel thiacyclopentane, [17]aneS₅-polymer, has been synthesized and used to successfully extract Hg²⁺ from acidic aqueous solution. The removal of Hg²⁺ from solution was determined to be 95% over a wide range of pH (1.5 to 6.1) and Hg²⁺ concentrations (4 to 200 ppm). The thiacyclopentane polymer is also selective for Hg²⁺ in the presence of competing metal ions. The polymer can be stripped of the Hg²⁺ and reused to extract more Hg²⁺. The thiacyclopentane appears to be unaffected by incorporation into the polymer, and the binding site of Hg²⁺ in the polymer has been identified to be similar to that of the non-polymer incorporated thiacyclopentanes, such as [15]aneS₅.

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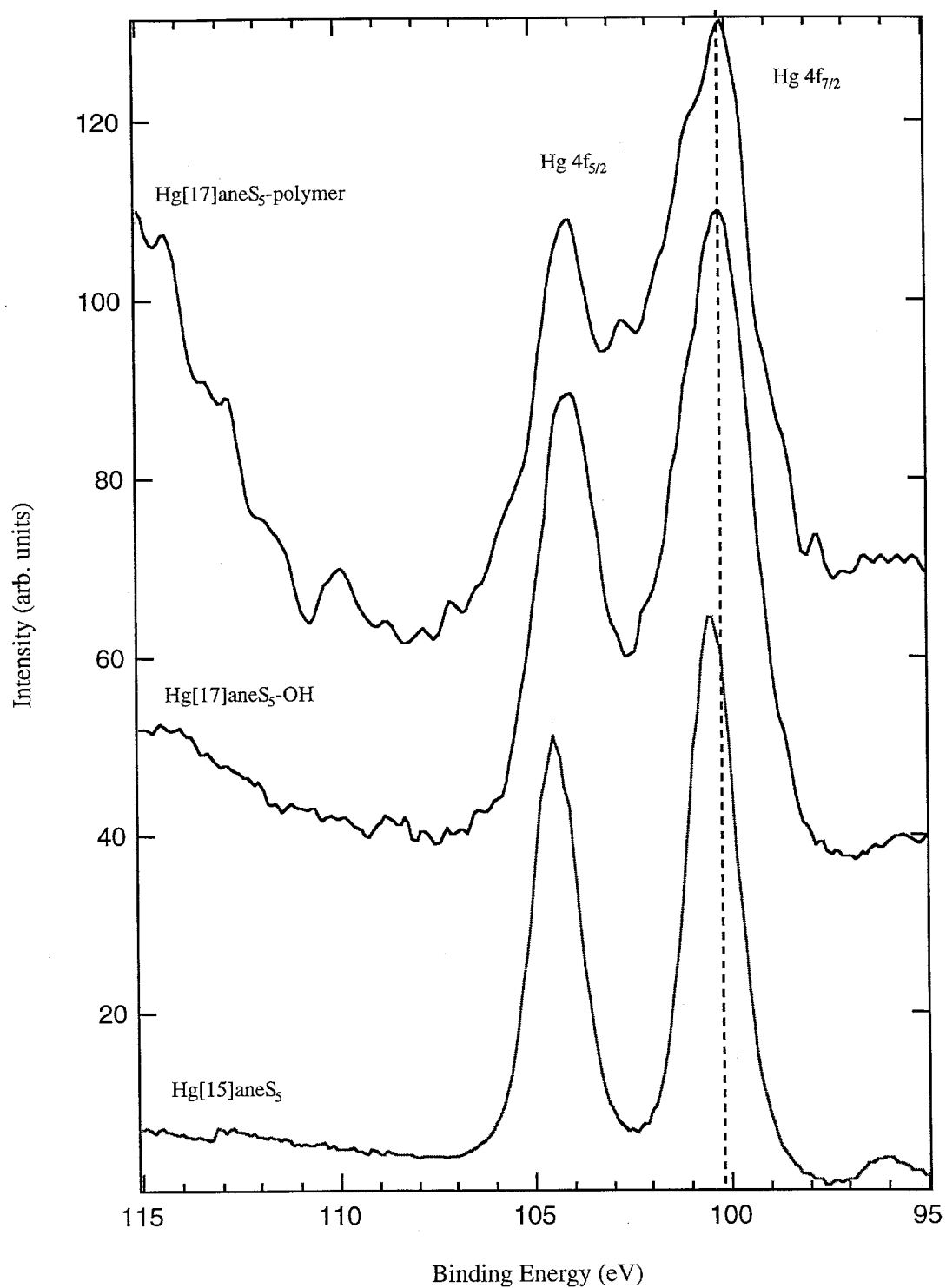


Figure 1 Hg 4f_{7/2,5/2} core-level spectra for Hg[17]aneS₅-OH, [17]aneS₅-polymer with Hg and Hg[15]aneS₅(PF₆)₂.

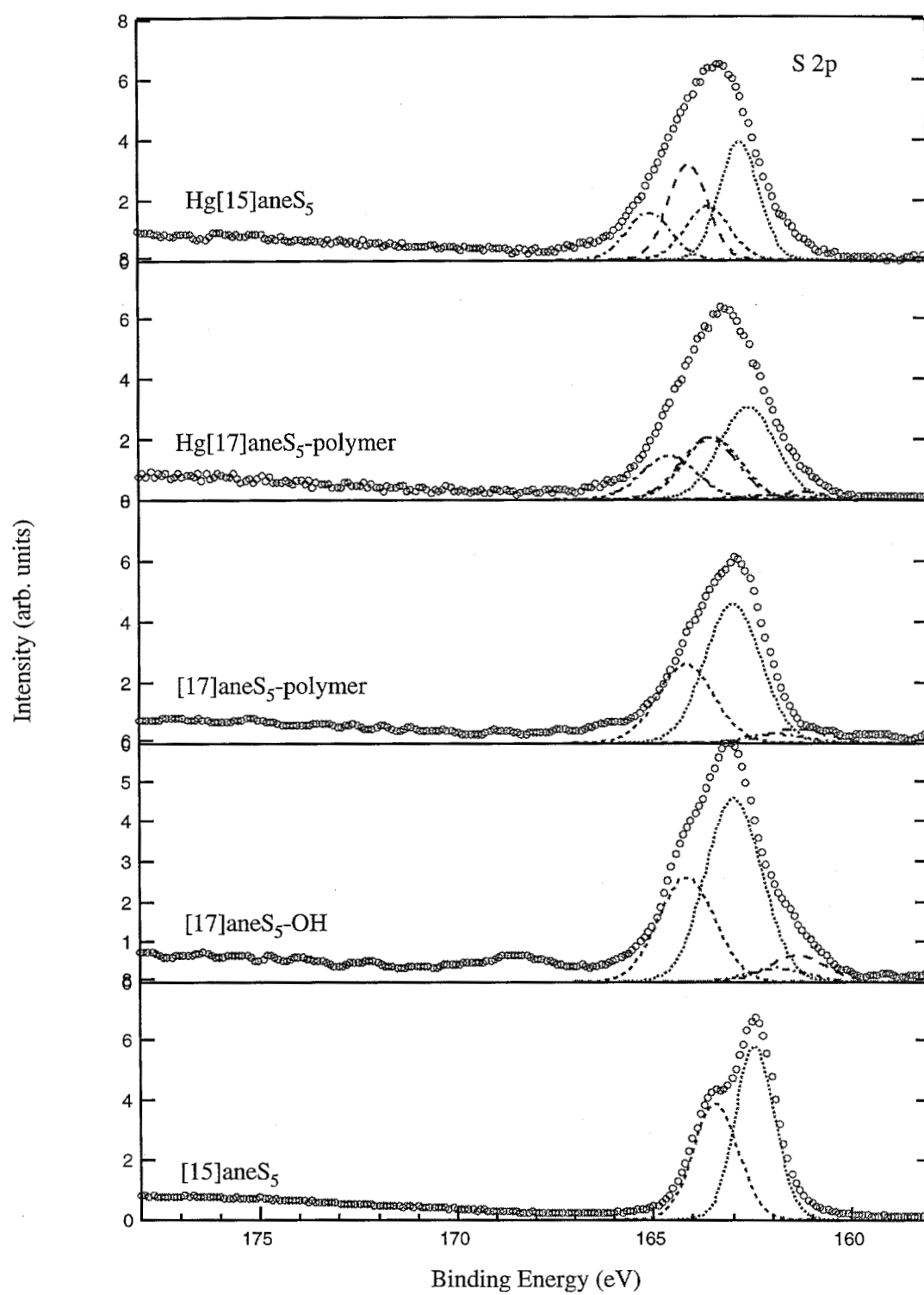


Figure 2. Deconvoluted high-resolution S $2p_{3/2,1/2}$ core-level spectra for [15]aneS₅, [17]aneS₅-OH, [17]aneS₅-polymer, [17]aneS₅-polymer with Hg, and Hg[15]aneS₅(PF₆)₂